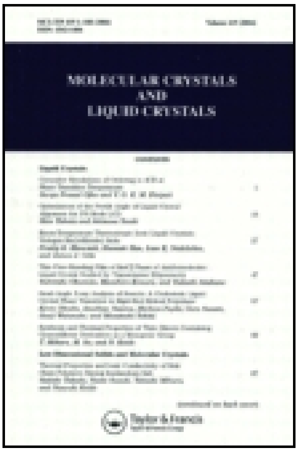

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Characterization of Phthalocyanine Langmuir-Blodgett Films by Optical Dichroism and Resonance Raman Scattering

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CHARACTERIZATION OF PHTHALOCYANINE LANGMUIR-BLODGETT FILMS BY OPTICAL DICHROISM AND RESONANCE RAMAN SCATTERING

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Abstract In this Paper we report optical dichroism and polarized resonance Raman scattering measurements on Langmuir-Blodgett layers of tetra tertiary butyl monosulphonic acid of phthalocyanine (tBPcSA). These measurements were performed to determine molecular alignment and local ordering in our samples, using surface enhanced optical and Raman spectroscopy. Thus our L-B layers were deposited on rough thin (50 Å) Ag island films. We found that the surface enhancement effects dominated the optical behaviour of our samples, making it more difficult to extract the desired information on molecular orientation. At the same time , we found that tBPcSA L-B layers can be a good system to study resonance effects and to test the reliability of the structural information obtainable by optical spectroscopic techniques.

INTRODUCTION

Surface Enhanced Raman Scattering (SERS) is a commonly used technique to obtain good and usable signals in the study of L-B mono- and multilayers by Raman spectroscopy [1]. Similar resonance effects can also be observed in optical or infrared absorption.

Raman scattering is a powerful, versatile technique to obtain information not only on vibrational dynamics, but also on local order and molecular orientation in the layers, and layer stacking and reproducibility. Thus it is useful to be able to obtain Raman spectra for L-B film characterization. From this point of view it becomes necessary to evaluate just how much the use of resonance enhancement techniques changes or selects the information that is seeked. In this Paper we try to do that by studying L-B layers of a new phthalocyanine derivative [2] by ordinary, resonant, SERS and SERRS

Raman spectroscopy, and by optical dichroism measurements. A preliminary report has already appeared [3]. Here we wish to discuss mainly our new results obtained with polarized light, both in optical absorption and in Raman measurements. In particular, we have studied optical dichroism in the phthalocyanine well known Q-band absorption and polarized SERRS as a function of sample orientation and the number of L-B layers.

EXPERIMENTAL TECHNIQUES

Sample Preparation

The L-B deposition of the tBPcSA molecule was performed using a Lauda through and microbalance, at a tension of 30 mN/meter. At such point in the isoterm the area per molecule was 90 Å^2, implying a molecular orientation relative to the subphase of about 75^o. The molecules were deposited on two different types of substrate: for the non-SERS measurements, on a hydrophobic glass slide. In this case Z-type layers were obtained. For the SERS configuration, the L-B layers were deposited on hydrophilic glass slides on which a 50 Å thick island film of Silver had been previously evaporated under high vacuum. We prepared samples with 1, 3, 5, 6, 7, 10 layers for the SERS configuration, and samples of up to 14 layers for the non-SERS configuration. Finally, a sample of 25 layers on a silicon wafer was prepared for FTIR characterization.

Spectroscopy

Optical absorption spectra were taken in ordinary transmission geometry with a computer controlled double beam spectrophotometer. The polarizer for the dichroic spectra was oriented at 0, 45, 90 degrees relatively to the dipping direction. The spectra were also taken with the sample dipping direction oriented at 0, 45, 90 degrees relatively to the laboratory vertical. Since in the spectral region of interest (the Q-band) the contribution to overall absorption due to the silver substrate is considerable, self-consistent subtraction procedures must be used to deal with such background, which varied from sample to sample, due to the intrinsically non-homogeneous character of the silver island films, and to the possible interaction between silver substrate and the first L-B layers.

Raman spectra were taken with a standard, computer controlled spectrometer in a backscattering geometry. Excitation was provided by the lines at 488 nm and 514.5 nm of an Argon laser, or was selected in the 590-690 nm range of a dye laser. In this latter case the incident light was filtered with a small monochromator to minimize unwanted spurious emission from the dye laser. Finally, the Infrared absorption spectra were taken with a Fourier Transform Interferometer in the thransmission geometry.

Since phthalocyanine is photosensitive, care must be taken that the excitation light does not modify or damage the sample. We studied in some detail the effect of light intensity on the Raman spectra using a double beam pump-probe arrangement [3]. We found that, using a rotating sample configuration, the sample could be irradiated with up to about 300 mW of light (cylindrical focussing) at 514.5 nm before showing visible spectral changes. Since however we also found this threshold to be sensitive to sample quality, in our measurements in the rotating sample configuration we never exceeded 60 mW. Such power level was reduced to 20 mW with cylindrical focussing for the measurement with a still sample. In any case care was always taken to check the time independence and reproducibility of our spectra. The L-B layers we prepared were of sufficiently high quality that no changes were observed in the spectra after one year and innumerable hours of exposure to laser radiation. All spectra reported here were taken, unless otherwise stated, with an integration time of 1 s/ch, and with a spectral bandpass of 3 cm^{-1}; they were not digitally filtered or smoothed.

RESULTS

Optical Absorption

In fig. 1a we show the behavior of the optical density maximum in the Q band as a function of the number of layers in the non-SERS configuration. A linear behavior is very nicely followed, with a slope of 0.008 per layer. In fig. 1b we show the same behavior for the SERS samples. Clearly there is a strong enhancement of the oscillator strength of the transition for the first layers (say up to the third), thereafter the normal linear behavior with the proper slope is followed.

In fig. 2 we show the dichroic spectra for the 14 layers sample in the non-SERS configuration. Clearly there is no appreciable dichroism in the Q band. If in the molecular frame we denote with x,y the molecular plane and with z the normal to such plane, the transition dipole moments connected with the Q band absorption would be directed along x or y, or in any case in the plane xy, depending on the degree of mixing of the Qx and Qy wavefunctions due to configuration interaction and solid state effects.

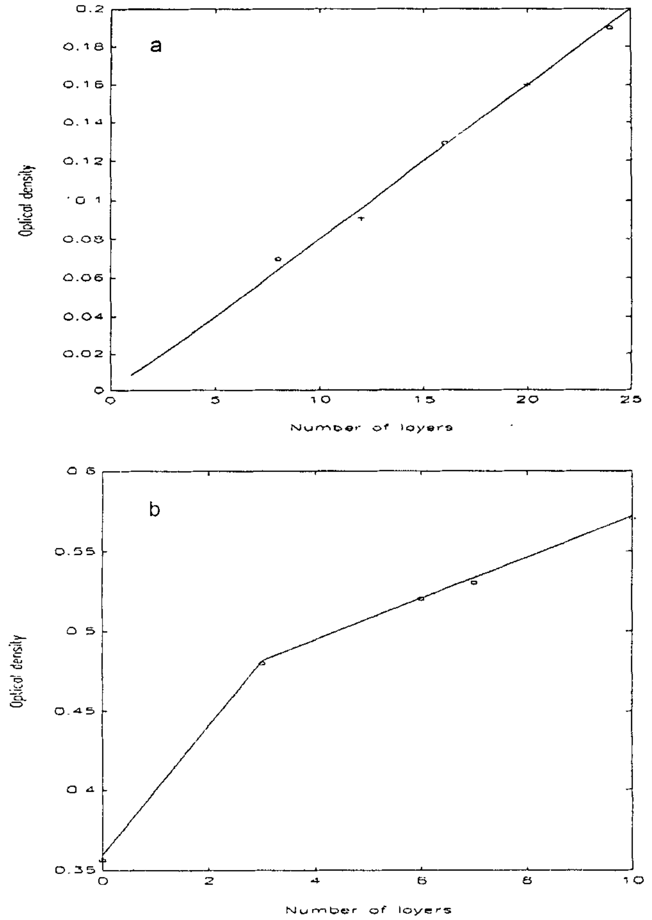

FIGURE 1. OPTICAL DENSITY AS A FUNCTION OF THE NUMBER OF LAYERS FOR A TBPCSA LB SAMPLE;
a)NON-SERS [GLASS SUBSTRATE]; b)SERS [GLASS PLUS AG ISLAND FILM SUBSTRATE].

Thus the absence of dichroism could indicate strong disorder in the molecular orientation, strong x-y mixing in the wavefunctions, or both. However it seems unlikely that wavefunction mixing be so strong as to eliminate all dichroism in our L-B samples, since for L-B layers of well oriented PC molecules a reasonably strong dichroism has been reported [4]. Thus the absence of dichroism in the non-SERS samples could probably be more related to orientational disorder connected with the presence of domains.

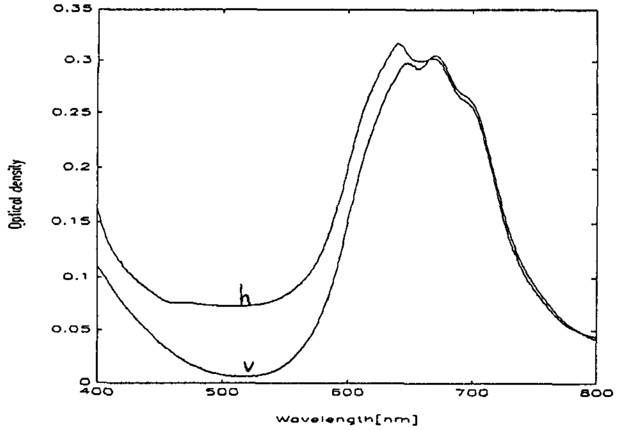

FIGURE 2. DICHROIC SPECTRA (VERTICAL (V) AND HORIZONTAL (H) POLARIZATION) OF THE 14 LAYERS SAMPLE [GLASS SUBSTRATE].

Very different is the behavior of dichroism in the SERS samples. Here the presence of the silver island films induces a strong dichroism, as can be seen in figs. 3, where we show the dichroic spectra for a 7 layers sample (silver background was subtracted), taken with the dipping direction of the sample respectively vertical (3a) and horizontal (3b), relative to the lab reference . The dichroism favors the horizontal polarization, **for both orientations**: thus it cannot be due to molecular orientational order. In such case in fact a sample rotation of 90° should lead to an inversion of the sign in the dichroism, which is clearly not observed. Thus the dichroism must be another manifestation of the resonance enhancement effect due to the interaction of the phthalocyanine layers with the silver island film. In such case in fact only the horizontal polarization ("p" component) would be favored.

The enhancement effects influence also the absorption spectrum. In fig. 3c and 3d we show the dichroic spectra of a 3 layers sample. Although the overall dichroism as measured by the band areas is about the same as for the 7 layers sample, we can observe a spectral change, namely, an increase in absorption at longer wavelengths: this indicates an increased intermolecular coupling [5], probably mediated by the plasma excitations in the silver film. Finally, the Q band appears clearly split in the absorption spectra of 3 layers sample; such structure broadens as the number of layers increases, indicating a weakening of the effects of resonance enhancement and possibly a parallel stronger role of interlayer-interaction.

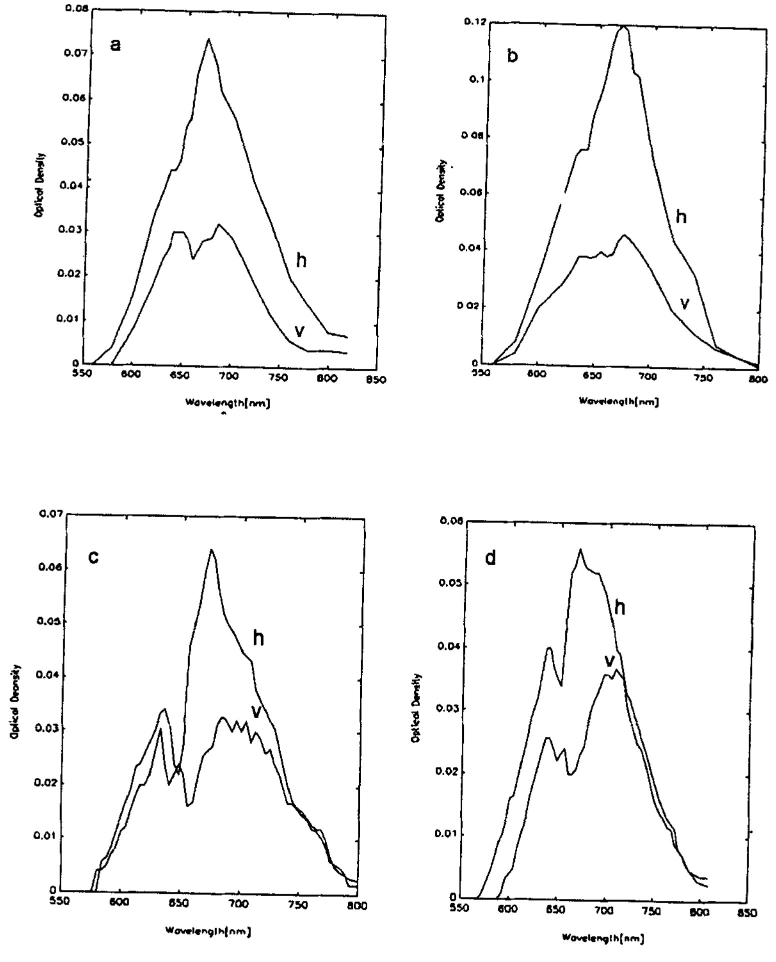

FIGURE 3. THE DICHROISM OF THE ABSORPTION SPECTRA OF A VERTICAL (a) AND A HORIZONTAL (b) 7 LAYERS SAMPLE AND OF A VERTICAL (c) AND A HORIZONTAL (d) 3 LAYERS SAMPLE.

Raman Scattering

Polarized Raman spectra taken in the SERRS configuration are shown in fig. 4 for the 7 layers samples. Excitation wavelength was near the peak of the phthalocyanine absorption, namely at 649 nm. The spectra were taken in a backscattering configuration with the incident light propagating at an angle of about 30° from the surface normal of the non rotating sample. The spectra are strongly polarized, furthermore the polarization ratio r is larger for the "horizontal"sample (for the 685cm^{-1} peak of the macrocycle vibration, r = 3 for the vertical sample and r = 4 for the horizontal sample orientation). We also note that the overall spectral intensity is about 20 % larger for the "horizontal" sample than for the "vertical" one.

We have also obtained polarized spectra in the SERS, out-of-resonance configuration (fig.5), for excitation at 514.5nm. The spectra are still polarized, however the overall degree of polarization is consistently smaller.

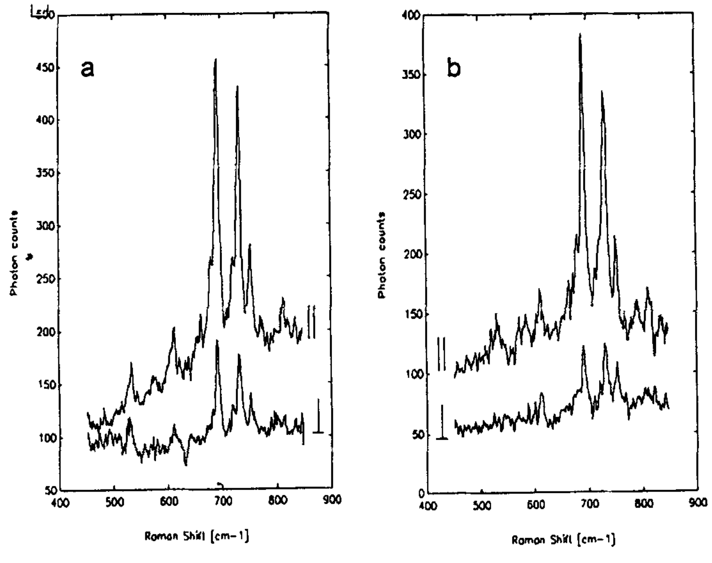

FIGURE 4. POLARIZED SERS (λo = 649 nm) SPECTRA FOR A HORIZONTAL (a) AND A VERTICAL (b) 7 LAYERS SAMPLE.

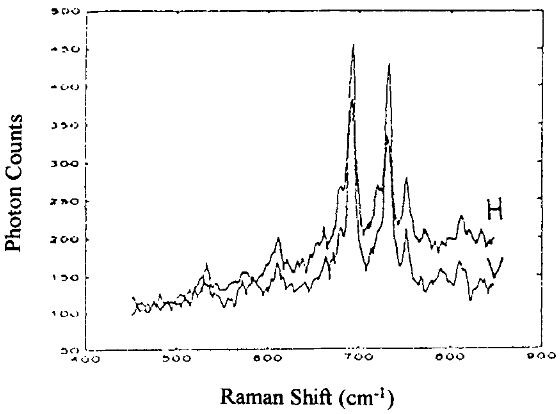

FIGURE 5. HORIZONTALLY POLARIZED RAMAN SPECTRA FOR VERTICAL (V) AND HORIZONTAL POSITION OF THE SAMPLE.

This implies that a degree of orientational order of the molecules must exist, since at resonance (SERRS configuration) the dipole selection rules which govern the electronic matrix elements involved in the Q-band absorption are expected to influence the scattering intensity, over and above the SERS enhancement.

On a polarized background due to the metal film and to tBPcSA luminescence our spectra show the characteristic peaks of phthalocyanine as reported in the literature [6,7]. We observed (fig. 5) a gradual decrease of the polarization ratio from the extended macrocycle vibrations to the more localized group vibrations at higher frequencies. Such behavior again may be related to SERS effects, since the macrocycle vibrations should be more strongly coupled to the electronic states which are mainly involved in the interaction with the silver substrate.

We wish to discuss now the spectral differences we found between the SERS and non-SERS samples, in and out of resonance. Let us discuss first the effects of resonance, i.e. the spectra taken in the SERS and SERRS configurations. In figs. 4 and 5 we have reported the relevant spectra. At resonance the 798 cm^{-1} peak almost disappears, while a new peak at 752 cm^{-1} increases; this is in agreement with the observations of ref. 6. However their 730 cm^{-1} peak relative intensity is about half the one we observe. This and other small differences are probably due to the different deposition method (evaporation) they use.

A most interesting difference between the SERS and SERRS spectra is the reversal of the intensity of the components of the so-called Davidov doublets [8] in the 1000-1600

cm^{-1} range as we go out of resonance. At resonance the scattering is specifically sensitive to the electronic wavefunctions of the resonating state; in the case of Pc, the Qx and Qy components of the Q band. Out of resonance instead such sensitivity is lost. Thus, the inversion is a clear indication of the preference for a specific vibrational symmetry as resonance with either of the Q band states is approached. This implies that the Qx and Qy states, although probably mixed by solid state effects, still retain enough of their character to enhance one of the components of the vibrational doublet, at least in the excitation range we explored. Clearly an extension of our measurements towards the infrared is needed to confirm this point. If confirmed however, this result would be strong evidence for a Davidov splitting of the molecular vibrations, and thus for the existence on the local level of two preferred molecular orientations. This would yield an alternative explanation to disorder for the lack of optical dichroism in our films, namely, a molecular distribution in which the nearest neighbor molecules are oriented essentially perpendicularly to each other, while keeping their 75° orientation relative to the substrate.

We have also obtained spectra in the non-SERS, resonant configuration (RRS) [3]. Such spectra are reasonably similar to the SERRS ones, including the sign of the Davidov splitting. This confirms that such an effect is not connected to the SERS enhancement, but instead is due to the resonance with the Q band electronic states.

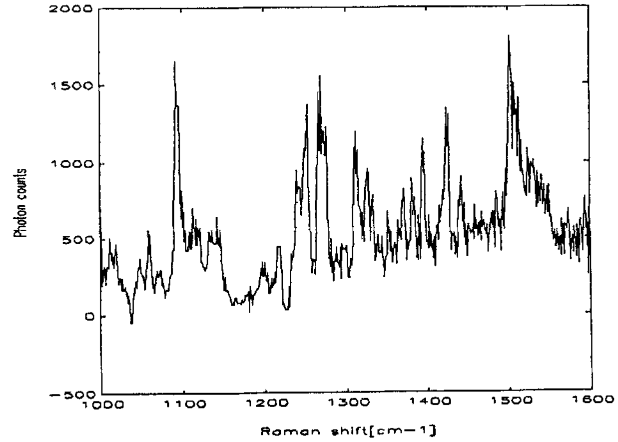

FIGURE 6. RAMAN SPECTRUM (NO RESONANCE, λ= 514.5nm, NO SERS) FOR A 15 LAYERS SAMPLE.

We come now to the spectra we have obtained in the absence of all resonance effects. In fig.6 we report the Raman spectrum taken in the non-SERS, out-of-resonance configuration, and in fig.7 we show the FTIR infrared absorption spectrum, taken in the ordinary transmission mode for a 25 layers sample deposited on silicon. We show only the region between 1000 and 1600 cm^{-1}, since for lower frequencies noise problems were too strong to obtain meaningful data. Further work on this is in progress.

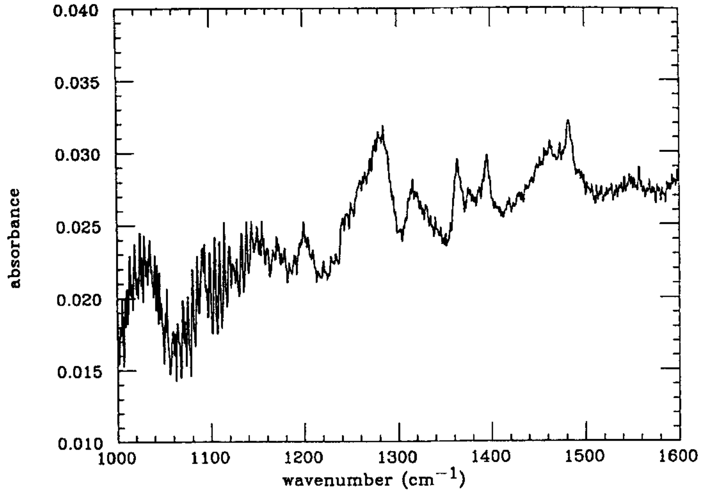

FIGURE 7. FTIR SPECTRUM OF TBPCSA DEPOSITED ON SILICON (25 LAYERS).

The Raman spectrum shown in fig.6 was obtained by cumulating several iterated spectra for a total integration time of 24 s/channel. The signal was almost completely due to the spectrum from the glass substrate, which in fig. 6 has been subtracted. The noise problem is so severe that only the strongest features should be considered. Note in particular the Davidov doublet in the 1500-1600cm^{-1} range, which has the same form as its counterpart in the non-resonant, SERS spectra. On a qualitative level, some of the main spectral features reproduce those found in the SERS or SERRS spectra. However, as should be expected, resonance effects do not enhance the intensity of many vibrational peaks, which are then "lost" . This is confirmed by comparison with the FTIR spectrum. In such spectrum we also note the approximate validity of the exclusion rule: the strong IR peaks are weak in the Raman spectra and viceversa. This indicates that not only the molecule, but also the multilayer structure retains an approximate inversion symmetry.

CONCLUSIONS

The Raman and optical dichroism data presented here show quite a complex picture for the structure and the interactions of LB films of tBPcSA, and of phthalocyanines in general. In particular we show that SERS-type effects can cloud information about molecular orientation to a considerable extent. From this point of view, only RRS should be used if possible. In any case, it is advisable to complement the data with results from IR absorption. In any case, the existence and resonance behavior of the Davidov doublets indicate two possible molecular orientations in the LB layer.

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